Quantitative Energy-Filtering Image of Carbon Nanotube (STATES AND STRUCTURES - Electron Microscopy and Crystal Chemistry)

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Energy-filtering transmission electron microscopy is applied to a single carbon nanotube in order to investigate quantitative property of elemental maps obtained by inelastically scattered electrons corresponding to the carbon K-edge. We find that the contrast differences due to 20 carbon atoms or to 6 graphene sheets are well observed in the carbon distribution image with a nanometer resolution.

Keywards: Elemental Map/ Electron Energy-Loss Spectroscopy/ TEM

Energy-selecting technique based on an electron energy-loss spectroscopy (EELS) in conventional transmission electron microscopy [1] provides energy-filtered high-resolution image and diffraction, and also elemental map, which promise quantitative analyses of specimens. In particular the elemental mapping makes it possible not only to visualize a two-dimensional distribution of a particular element, but also to count the number of atom existing in a specific region by analyzing the intensity of image quantitatively. In order to investigate the quantitative property of an elemental map, a thin specimen is needed because multiple scattering of electrons disturbs the intensity distribution. Here we report the usefulness of this technique for obtaining quantitative elemental distribution for the case of carbon nanotubes.

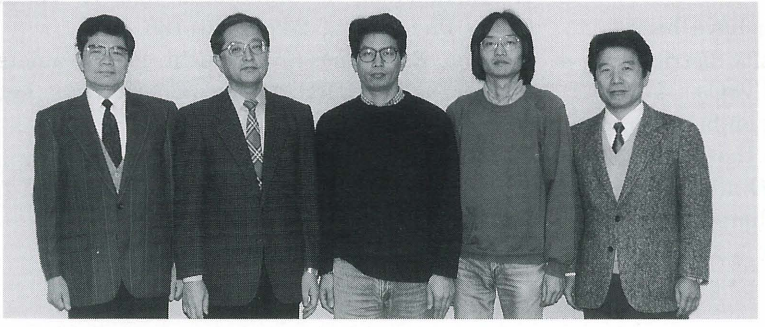
The structure of carbon nanotube is characterized by the inner and outer diameters of a tube and the number of graphene sheets [2]. Typical diameter of a tube is the order of nanometer which is thin enough to analyze the intensity of the elemental distribution image without any corrections on multiple scattering. Since the structural parameters of each nanotube can be determined definitely from a high-resolution electron micrograph, the carbon distribution image observed from a well-defined nanotube is very suitable for examining the quantitative property of the elemental mapping. The investigations were performed using the 1MeV atomic resolution electron microscope (JEOL) [3] equipped with a Gatan imaging filter (GIF) [4].

High resolution lattice image and carbon distribution image of self-supported nanotubes were observed at a magnification of the microscope of 20,000x which corresponds to an effective magnification of 340,000x on the slow-scan CCD camera of the GIF. This means that the pixel size referred back to the objective plane is 0.07nm which allows us to observe the elastic image of the (002) lattice planes (d=0.34nm) of graphite. This magnification is, therefore, enough to characterize the structure of each nanotube by imaging graphene layers. In the carbon distribution images, however, the intensities of 4x4 pixels were integrated into one effective pixel (binning mode) because of the small

STATES AND STRUCTURES — Crystal Information Analysis —

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of orgainc materials, and development in high resolution electron spectromicroscopy including electron energy-loss spectroscopy.



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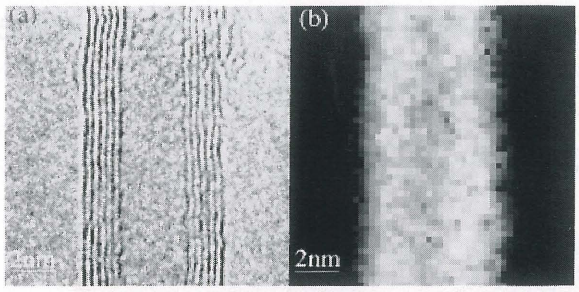

Figure 1. (a) High-resolution lattice image of a single nanotube and(b) corresponding carbon distribuition image.

inelastic scattering cross-section of the carbon K-edge compared to that of elastic scattering, so that the effective pixel size became 0.28nm.

Typical high-resolution lattice image of a single nanotube and its carbon distribution image formed with electrons lost their energy by exciting the K-shell of carbon are shown in Figure 1a and 1b, respectively. The lattice image clearly indicate the 6 layered cylindrical structure. The outer and inner diameters of the tube are 6.5nm and 3.15nm, respectively. Figure 2 shows the intensity profile of carbon distribution image across the tube axis in which the intensities measured are plotted by the open circles. The intensity of the carbon profile increases from the vacuum to the inside of the tube, which indicates the increase of the number of carbon atom. The intensity maxima separated with a distance of 3.1nm are observed in the line profile. Here, we relate quantitatively such a characteristic carbon profile to the atomic distribution determined by the following procedure.

Within the thin film approximation, the image intensity at each pixel of the detector is proportional to the number of carbon atoms projected on each pixel of the detector. The proportional constant is related to the electron dosage irradiated on the specimen, the partial inelastic scattering cross-section of carbon K-edge and the conversion efficiency of the detector system. These values were determined: the electron dosage was measured to be 1.25×10^7 electron/nm^2 and the inelastic scattering cross-section was calculated using the SIGMAK software [5] with the collection angle of 10mrad and the energy window of 30eV. Since the incident electron energy is 1MeV, relativistic correction for the inelastic cross-section was included in the present calculation. The conversion efficiency of the detector system is 0.3 in the present device. The number of carbon atom projected on each pixel of the detector can be simply estimated by assuming the 6 layered cylindrical structure observed in Figure 1a.

The agreement of the experimental and theoretical intensity profiles is quite satisfactory (Figure 2), which means the elemental distribution image is highly quantitative as long as a thin specimen is examined. The intensity maxima and minimum at the central region of the nanotube correspond to about 50 and 30 carbon atoms per pixel, respectively. Therefore, we conclude that the difference of 20 carbon atoms can be detected at nanometer scale with a good signal to noise ratio.

Similar observation and analysis have been performed on the conical tip region of a nanotube. The lattice image shows that the tip is made by progressive multilayer of curved graphene sheets [6].

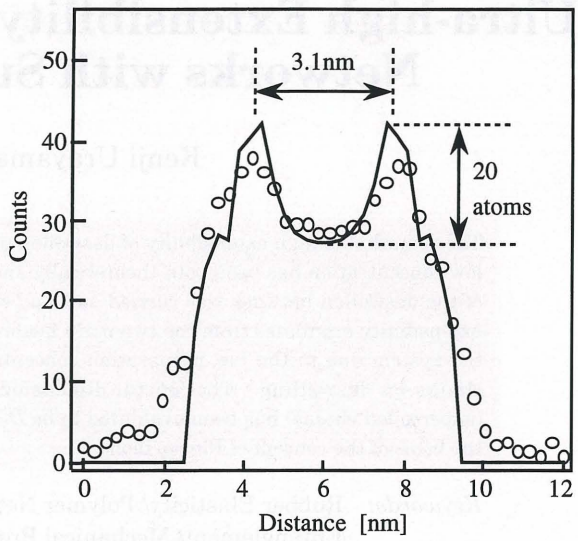

Figure 2. Comparison between the experimental intensity profile of carbon distribution image and the calculated one.

In one case the numbers of layers are 5, 8 and 14 layers from the tip to inside of the tube. Since the tip has a conical symmetry about the cone axis, the number of carbon atoms is constant in the respective multilayer regions. Such the distribution of the carbon atoms was visualized by the elemental mapping. The intensity profile along the cone axis showed the stepwise intensity change from the tip to inside of the tube as expected from the increase of graphene layers. The differences of the step height in the line profile correspond to 6 and 12 graphene layers, respectively, because the electron beam travels through the upper and lower multilayers of the nanotube. Such differences of the graphene layers are equivalent to 18 and 36 carbon atoms per pixel, respectively. In this example, therefore, we can also detect the difference of about 20 carbon atoms.

Our observations [7] establish that the energy-filtering technique based on EELS is very powerful to analyze the elemental distribution quantitatively with a nanometer resolution. For the ultimate single atom analysis it should be necessary to irradiate much stronger electron beam than the present experiment. However, the nanotubes suffer structural distortion from intense electron irradiation, so that the observed detection limit is restricted by the stability of specimen to electron beam.

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